

TITLE OF THE INVENTION

Mixed Conductor and Mixed Conductor Producing Method

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to a mixed conductor which exhibits both electronic conduction and proton conduction. This mixed conductor can be used for the catalyst layer of a fuel cell, a gas diffusion catalyst and the like.

10 2. Description of the Related Art

The catalyst layer of a fuel cell is formed between a proton exchange membrane and a backing layer and supports a catalyst for accelerating an electrochemical reaction. A combination of the catalyst layer and the catalyst layer constitutes the electrodes of the fuel cell. In the catalyst
15 layer on an air cathode side, for example, protons passing through the proton exchange membrane and electrons transferred to the air cathode are conducted up to the catalyst, thus binding oxygen and protons diffused onto the catalyst. Namely, the catalyst layer needs to exhibit both proton conduction and electronic conduction in order to improve the transfer loss of
20 oxygen, protons and electrons. To this end, a mixture of poly electrolyte having catalysts supported on surfaces such as carbon particles (exhibiting electronic conduction) and Nafion (trade name, manufactured by E.I du Pont de Nemours, this applies hereafter) which exhibits ionic conduction is used in the fuel cell.

25 However, if a material having ionic conduction and a material having electronic conduction are used together, it is difficult to mix them up completely uniformly. As a result, protons and electrons cannot be

uniformly transferred to all catalyst particles.

To solve this disadvantage, there has been proposed a mixed conductor which exhibits both ionic conduction and electronic conduction using one material.

5 For example, organic mixed conductors are disclosed in the following patent documents 1 to 4.

In addition, inorganic mixed conductors conducting electrons and oxygen ions are disclosed in the following patent documents 5 to 8.

Patent Document 1: Japanese Unexamined Patent Publication No.
10 2001-202971

Patent Document 2: Japanese Unexamined Patent Publication No.
2001-110428

Patent Document 3: Japanese Unexamined Patent Publication No.
2003-68321

15 Patent Document 4: Japanese Patent Application National Publication (Laid-Open) No. 2002-536787

Patent Document 5: Japanese Unexamined Patent Publication No.
(10)1998-255832

Patent Document 6: Japanese Unexamined Patent Publication No.
20 (11)1999-335165

Patent Document 7: Japanese Unexamined Patent Publication No.
2000-251533

Patent Document 8: Japanese Unexamined Patent Publication No.
2000-18811

25

Since the organic mixed conductors are made of organic materials, they have many problems in terms of durability and heat resistance to be

solved before being put to practical use.

As for the inorganic mixed conductors which transfer electrons and oxygen ions, operating temperatures thereof are high (about 800°C). Due to this, it is considered that these inorganic mixed conductors are
5 inappropriate for small-sized fuel cells suitably used in, for example, vehicles and cellular phones.

SUMMARY OF THE INVENTION

After exerting utmost efforts in study to solve these disadvantages,
10 the inventor of the present invention discovered a novel inorganic mixed conductor and finally completed the present invention.

That is, the inventor of the present invention discovered a mixed conductor characterized in that an electron conductor made of an inorganic material is fixed to a proton conductor made of an inorganic material so as
15 not to dissolve in water.

As the electron conductor made of an inorganic material, an electron conductor of such a type as to cause a main chain to have one of or both of a carbon-carbon double bond and a carbon-carbon triple bond, the main chain contributing to an electronic conduction function as shown in Figs. 1 and 2.
20 may be used or such a type as to transfer electrons through a side chain.

It is also preferable that such an electron conductor uses an inorganic material obtained by carbonizing an organic compound having a π bond. Examples of the organic compound having a π bond include aliphatic hydrocarbon, aromatic hydrocarbon and derivatives of the aliphatic
25 hydrocarbon and the aromatic hydrocarbon. At least one of them is used for the organic compound having the π bond. Typical examples of the organic compounds include polyacetylene, resorcinol, phenol, phenylphenol,

polyaniline, polypyrrole, polythiophene, phenylphosphonic acid, and phenylsilane alkoxide.

Further, the inorganic material for the electron conductor can be a carbonaceous material such as graphite or a carbon nanotube or a metallic
5 material containing a metal such as gold, palladium, platinum, magnesium, lithium or titanium, or an alloy thereof.

As the proton conductor made of an inorganic material, one of a phosphorus-containing compound, a sulfur-containing compound, carbonic acid, boric acid, and inorganic solid-state acid, particularly at least one of a
10 phosphorus-containing compound, phosphoric acid, phosphoric ester, sulfuric acid, sulfuric ester, tungsten oxide hydroxide, rhenium oxide hydroxide, silicon oxide, tin oxide, zirconia oxide, tungstophosphoric acid, and tungstosilicic acid can be used.

According to the present invention, the inorganic electron conductor
15 and the inorganic proton conductor are fixed to each other so as not to dissolve in water.

They may be fixed by a covalent bond, intercalation or inclusion. However, depending on production process conditions, these manners of fixing may possibly be mixed.

20 Further, whether the state of fixing is by covalent bond, intercalation or inclusion is set according to the types of the materials of the electron conductor and the proton conductor. For example, if the electron conductor is made of an inorganic material obtained by carbonizing an organic material, the fixing may be made mainly by a covalent bond. If the
25 electron conductor is made of a metal material and an inorganic material, particularly an oxide is selected as a material for the proton conductor, for example, the both conductors can be fixed to each other by a covalent bond

or inclusion.

The state in which the electron conductors and the proton conductors are fixed to each other by a covalent bond is illustrated in Figs. 1 and 2. Since the electron conductors 1 or 3 and the proton conductors 2 bound by a covalent bond are arranged in close proximity, both the electron conductors and the proton conductors can contact with a catalyst particle (e.g., platinum) in nano order as shown therein. Accordingly, it is possible to supply electrons and protons necessary for a catalytic reaction to the catalyst in proper quantities.

10 Such a mixed conductor is formed as follows.

First, a precursor obtained by dispersing a proton conductor into a polymer of an organic compound having a π bond is prepared.

The precursor having a proton conductor dispersed into the polymer of an organic compound, or the precursor having both a proton conductor bound to an organic compound that constitutes the electron conductor by a covalent bond and a proton conductor separated from the former proton conductor and substantially in a dispersed state.

Further a high molecular precursor may be formed by polymerizing an organic compound having a π bond with a proton conducting material. In this high polymer precursor, it is considered that carbons mainly constituting the organic compound are polymerized with one another to form an electron conducting main chain having a π bond and also form a covalent bond with the proton conductor, and that this proton conductor bridges the carbon main chain of the electron conductor. By mixing the proton conductor in sufficient quantities, the distance between the proton conductors bound to the carbon main chain by covalent bonds is narrowed, and proton conduction is generated between the proton conductors.

According to research by the inventor, putting the polymer precursor in a solution of hydrolytic cleavage at 100 to 200 °C for several hours promotes to form covalent bond between the electron conducting main chain and the proton conductor. It causes improvement on proton conductivity and prevention for releasing the material of proton conductivity from the polymer precursor.

This precursor is pyrolysis under an inert atmosphere. As a result, the organic compound is carbonized into an inorganic material, thereby ensuring electronic conduction.

In addition, the proton conductor is stably fixed to the electron conducting carbon skeletons. As a result, proton conduction is ensured. It is considered that the proton conduction is attained by arranging proton conductor allocation materials to be proximate to each other. As shown in Figs. 1 and 2, if the proton conductors bridge the carbon skeletons, the positions of the proton conductors are fixed, thereby ensuring the proton conduction by the interaction between the proton conductors.

If the proton conductors are released from the carbon skeletons or if the proton conductors are not bound to the carbon skeletons from the state of the precursor, then it is considered that the proton conductors are intercalated into the carbon main chain or included in a mesh structure formed by the carbon main chain. In any case, it is considered that the proton conduction can be ensured as long as the proton conductors are in proximity.

As can be seen, since the proton conductors are bound, intercalated or included between the carbon skeletons, the proton conductor does not float. Due to this, even if the mixed conductor is used at a location where

water is present, the proton conductor does not flow out by the water. That is, a rate of lowering the proton conduction by water is very low.

Now, examples of the organic compound having a π bond include unsaturated aliphatic hydrocarbon and aromatic hydrocarbon. More concretely, at least one of polyacetylene, resorcinol, phenol, phenylphenol, polyaniline, polypyrrole, polythiophene, phenylphosphonic acid, and phenylsilane alkoxide can be selected as a material for the organic compound having a π bond.

Further, examples of the proton conducting material include a phosphorus-containing compound, a sulfur-containing compound, carbonic acid, boric acid, and inorganic solid-state acid. Examples of the phosphorus-containing compound include phosphoric acid and principle examples of the sulfur-containing compound include sulfuric acid and sulfonic acid. Further, an inorganic proton conducting material can be produced using a derivative of one of these compounds as a starting material. In this case, particularly at least one of a phosphorus-containing compound, phosphoric acid, ester phosphate, sulfuric acid, ester sulfate, sulfuric acid, tungsten oxide hydroxide, rhenium oxide hydroxide, silicon oxide, tin oxide, zirconia oxide, tungstophosphoric acid, and tungstosilicic acid can be used.

To mineralize the organic compound in the precursor, it is preferable that the precursor is burned under an inert atmosphere.

The inert atmosphere can be attained by putting the precursor under the distribution of nitrogen gas or helium gas or in vacuum.

If the precursor is pyrolysis under such an inert atmosphere, the organic component of the precursor is carbonized into an inorganic material. If the main chain of the organic component has a π bond, high electron

conduction is ensured.

Heating temperature and heating time are appropriately selected according to the characteristics of the precursor.

Simultaneously with or after heating, a high energy other than heat
5 can be applied to the precursor. Examples of the high energy include plasma radiation, microwave radiation and ultrasonic radiation.

As described above, the mixed conductor according to the present invention is made of inorganic materials and exhibit both an electron conducting function and a proton conducting function. In addition, even in
10 a low temperature range close to a room temperature, the mixed conductor functions properly. Further, even if water is present, the mixed conductor exhibits both electron conduction and proton conduction.

BRIEF DESCRIPTION OF THE DRAWINGS

15 Fig. 1 is a typical view illustrating the structure of a mixed conductor according to the present invention;

Fig. 2 is a typical view illustrating the structure of the mixed conductor according to the present invention;

Fig. 3 is a typical view illustrating the structure of the mixed
20 conductor in one embodiment according to the present invention;

Fig. 4 is a typical view of a holder for checking the proton conducting function of the mixed conductor in the embodiment;

Fig. 5 is a chart showing the current-voltage characteristics of the holder shown in Fig. 4; and

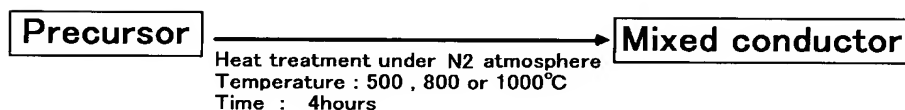
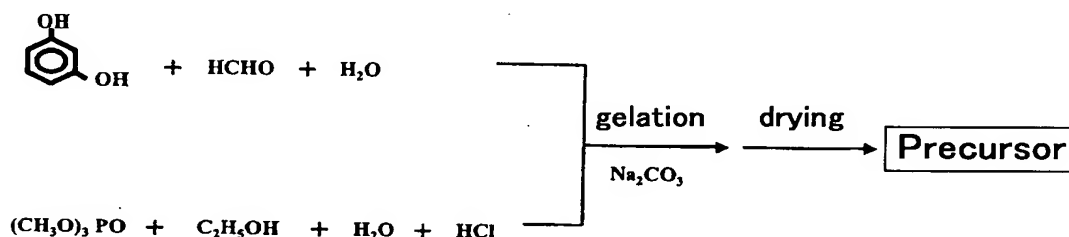
25 Fig. 6 is a chart showing the change of a phosphoric acid remaining rate with time in the mixed conductor in pure water in the embodiment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The above-stated advantages of the mixed conductor according to the present invention will be confirmed hereinafter by way of exemplary embodiments.

First, a method for producing a mixed conductor will be described with reference to the following chemical formula 1 as well as Fig. 3.

Chemical formula 1



Resorcinol (10 g) and formaldehyde (13 ml) are dissolved in water (40 ml), and a solution obtained by hydrolyzing trimethyl phosphate is added to the solution. The solution is subjected to reflux at 100 to 200°C for four hours and covalent bond between electron conductor and proton conductor in the solution is promoted. The resultant solution is dehydrated and condensed with Na_2CO_3 as a catalyst to gelate the solution. This gel is dried at 120°C, thereby obtaining a precursor.

This precursor is subjected to a pyrolysis (at 500 to 1000°C) under a

nitrogen atmosphere to obtain a mixed conductor in the embodiment. This mixed conductor is constituted so that electronic conductor phases 7 of a graphite-like structure and proton conductor phase 9 containing phosphoric acid group are alternately aligned as shown in Fig. 3.

5 The mixed conductor thus obtained is ground, pressed into a plate, and put between current collecting plates to supply a DC current to the plate-formed mixed conductor. Specific resistance of each embodiment is obtained from a voltage at that time. Measurement temperature is a room temperature.

10

	Embodiment 1	Embodiment 2	Embodiment 3
Heat treatment temperature	500°C	800°C	1000°C
Specific resistance (Ω cm)	138	0.35	0.13

15 In the embodiments, the reason of high specific resistance at a heating temperature of 500°C is considered to be insufficient carbonization of an organic material.

The heating temperature and heating time are parameters that can be appropriately selected according to the structure and the like of the organic compound.

20 Next, a proton conduction test will be described with reference to Figs. 4 and 5.

As shown in Fig. 4, a backing layer 17 consisting of a carbon cloth and catalyst layer 15 is attached to each side of a sample 11 in each of Embodiments 1 to 3. A Nafion membrane 13 transmits protons but blocks

electrons.

A holder shown in Fig. 4 is put in a container, and nitrogen gas or hydrogen gas at a temperature of 60°C and a relative humidity of 100% is introduced into the container. A voltage-current characteristic at that time is shown in Fig. 5.

As can be seen from Fig. 5, even if a voltage is supplied between the backing layers 17 while introducing the nitrogen gas, no current is carried. On the other hand, if hydrogen gas is introduced into the container, it can be seen that a current flows. This demonstrates that the sample 11 has proton conduction.

Further, the proton conductivity of each sample is calculated as follows.

	Embodiment 1	Embodiment 2	Embodiment 3
Heat treatment temperature	500°C	800°C	1000°C
Proton conductivity (S/cm)	2.6×10^{-3}	1.3×10^{-3}	7.3×10^{-4}

Further, as comparative examples, the proton conductivities of samples similarly subjected to a heat treatment by the formation method in the embodiments already described above and to which trimethyl phosphate are not added are calculated as follows.

	Comparative Example 1	Comparative Example 2	Comparative Example 3
Heat treatment temperature	500°C	800°C	1000°C
Proton conductivity (S/cm)	1.0×10^{-6} or less	1.0×10^{-6} or less	1.0×10^{-6} or less

By comparing the samples to which trimethyl phosphate is added with those to which trimethyl phosphate is not added, the appearance of proton conduction by phosphorus is proven.

5 The relationship between immersion time and phosphorus remaining rate when samples (0.1 g) in the respective embodiments are immersed in 1000 cc of pure water at a room temperature is shown in Fig. 6.

In Fig. 6, the phosphorus remaining rate is measured by an EDX analyzer.

10 The result shown in Fig. 6 confirms that about 60% of phosphorus, about 80% of phosphorus, and about 90% of phosphorus (i.e., proton conduction) remains in the samples in Embodiments 1, 2, and 3, respectively.

This demonstrates that the mixed conductors in the embodiments
15 keep their proton conducting functions even in a humid environment for a long time.

The mixed conductors can be used for fuel cells, and particularly suitably used for the catalyst layers constituting the respective fuel cells. The catalyst layer is a location where oxygen or hydrogen supplied from the
20 outside through the backing layers is ionized, and is normally arranged between the proton exchange membrane and the backing layer.

Examples of a method for producing a catalyst layer if one of the mixed conductors is used as the catalyst layer will next be described.

(Example 1)

25 Each of the mixed conductors produced above is ground to powder by a ball mill or the like, and the mixed conductor thus ground is caused to support a platinum catalyst. The mixed conductor can be made to support

the platinum catalyst by the same method as that for causing a carbon holder in a process of forming a supported platinum carbon that constitutes the catalyst layer of an ordinary fuel cell to support a platinum catalyst. For example, chloroplatinic acid solution is impregnated with the mixed conductor powder and then subjected to a reducing treatment, whereby the mixed conductor can support platinum catalyst.

The supporting mixed conductor is mixed into a Nafion solution, a paste of a mixture thereof is produced, and this paste is screen-printed on each surface of an proton exchange membrane (a Nafion membrane in this example). As a result, a catalyst layer containing the mixed conductor is formed. Further, a backing layer is connected to the outside of the catalyst layer, whereby a unit fuel cell that constitutes the fuel cell, i.e., a unit cell can be produced.

(Example 2)

Each of the mixed conductors produced above is ground to powder by a ball mill or the like, and the mixed conductor thus ground is caused to support a platinum catalyst.

Next, the powder of the mixed conductor which supports the catalyst is subjected to hot pressing, thereby forming the mixed conductor into a shape corresponding to a target electrode to produce a catalyst layer. This catalyst layer is superposed on the proton exchange membrane and hot press is conducted, whereby an integral formed article having the proton exchange membrane put between the catalyst layers is produced.

By further connecting a backing layer to the outside of the catalyst layer, a unit cell of the fuel cell can be produced.

In the tests stated above, the mixed conductors in the examples exhibit both proton conduction and electronic conduction at a low

temperature in a range of a room temperature to 60°C. Depending on the presence of water, it is considered that the mixed conductors exhibit the equivalent functions up to 200°C under an atmosphere.

5 It is seen that the mixed conductors in the embodiments can exhibit their functions even at an extremely low temperature as compared with the conventional inorganic-based mixed conductor which exhibits its functions at a high temperature of about 800°C.

10 Furthermore, as is obvious from the structure shown in Fig.3, the electronic conductor phase 7 is connected to the proton conductor phase 9 by a covalent bond, so that they are quite proximate to each other. Due to this, even if a catalyst particle is very small, the electron conductor 7 and the proton conductor 9 can be always brought into contact with the catalyst particles simultaneously. This makes it possible to supply electrons and protons necessary for a catalytic reaction to the catalyst in proper quantities
15 and thereby improve catalyst utilization efficiency.

The present invention is not limited at all by the embodiments and the description of the embodiments. The present invention also contains various changes and modifications thereto without departure from the description of claims which follow in a range that can be easily attained by a
20 person having ordinary skill in the art.